

Adding Value to Corn Dry Milling Distillers Grains

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2004 Ethanol Production Facilities



Renewable Fuels Association, 2005; <http://www.ethanolrfa.org/outlook2005.pdf>

2004 Fiber Production

	2004 Ethanol (Billion gallons)	2004 Fiber (million metric tons)
Dry Mills	2.55	7.30 distillers grains
Wet Mills	0.85	0.43 gluten meal 2.36 gluten feed

Goal

- Design selective chemical catalysts for the conversion of DDG components
- First system:
 - Hydrolysis of oligosaccharides

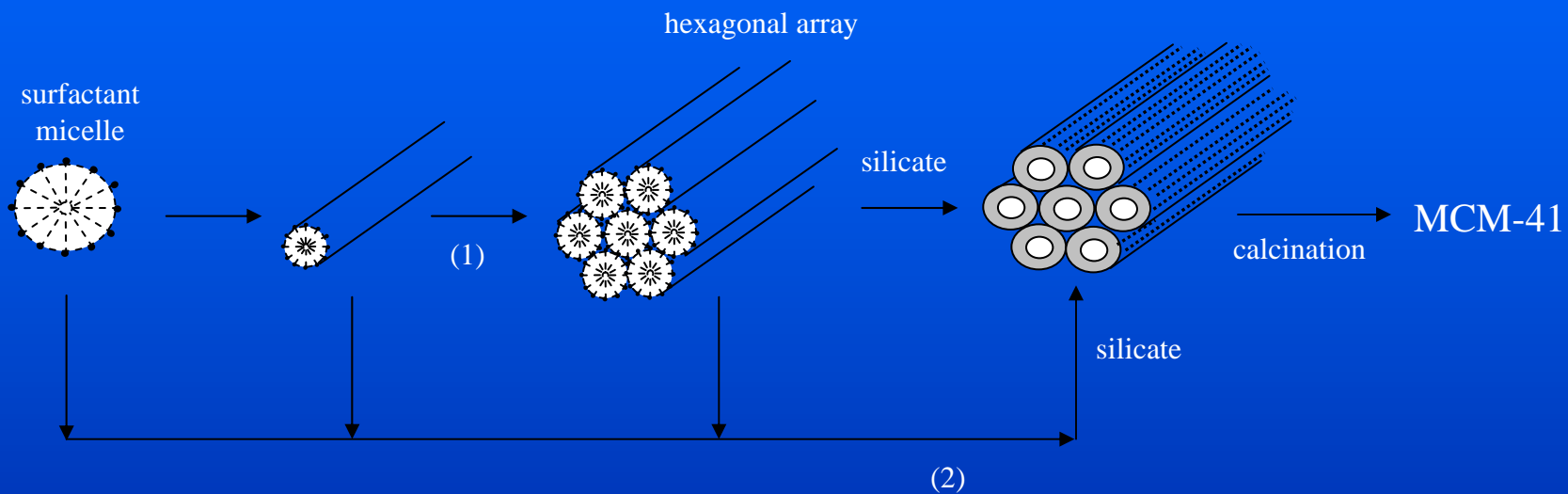
Midwest Consortium for Sustainable Biobased Products and Energy

- *Purdue University* - Michael Ladisch, Randy Woodson, Nathan Mosier, Wally Tyner
- *Iowa State University* – Brent Shanks
- *Michigan State University* – Bruce Dale
- *University of Illinois* - Hans Blaschek
- *USDA NCAUR* - Mike Cotta, Bruce Dien
- *Ames Laboratory* - John Verkade
- *Argonne* - Seth Snyder, Jim Frank

Consortium Overall Goals

1. Conduct research on the pretreatment fundamentals, enzyme catalysts, and microbial systems for converting both starch and cellulosic materials to ethanol at conditions consistent with the operation of a dry mill, including economic models;
2. Carry out fundamental studies on the structure and function of hydrolytic enzyme, biomimetic, and organic catalysts with respect to the structure and function of the cellulose and hemicellulose in corn fiber and corn stover that enhances their conversion to sugar; and where it makes sense;
3. Partner with regional ethanol producers and government agencies to achieve sustainable systems for renewable bioenergy and bioproducts by defining engineering fundamentals for utilizing lignocellulosics and fiber materials as feedstocks in dry mills.

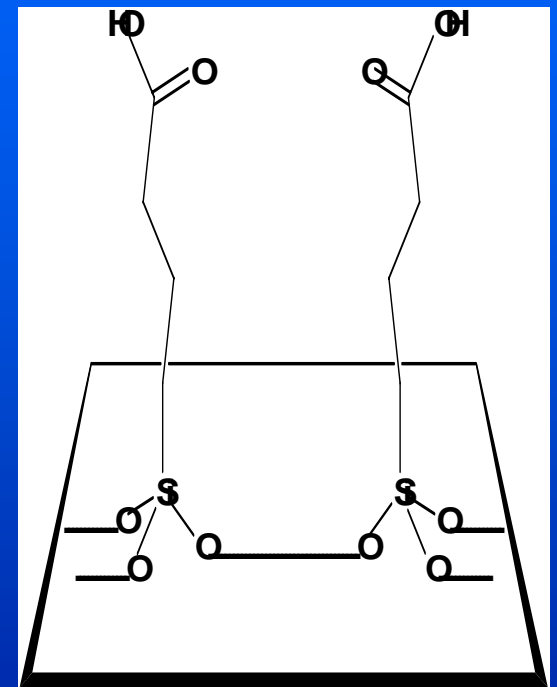
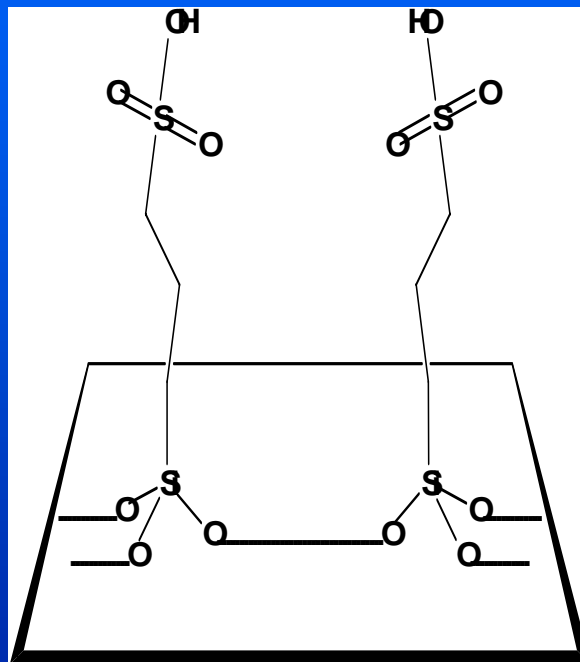
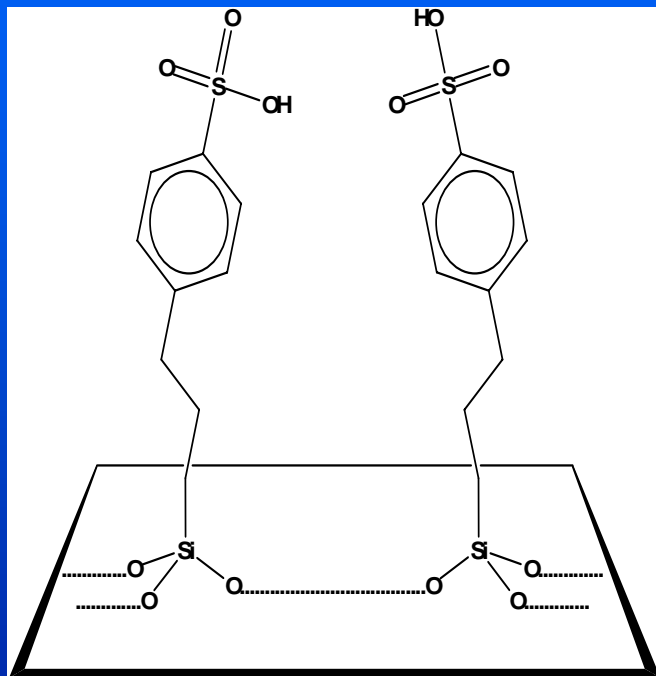
LCT Mechanism for MCM-41



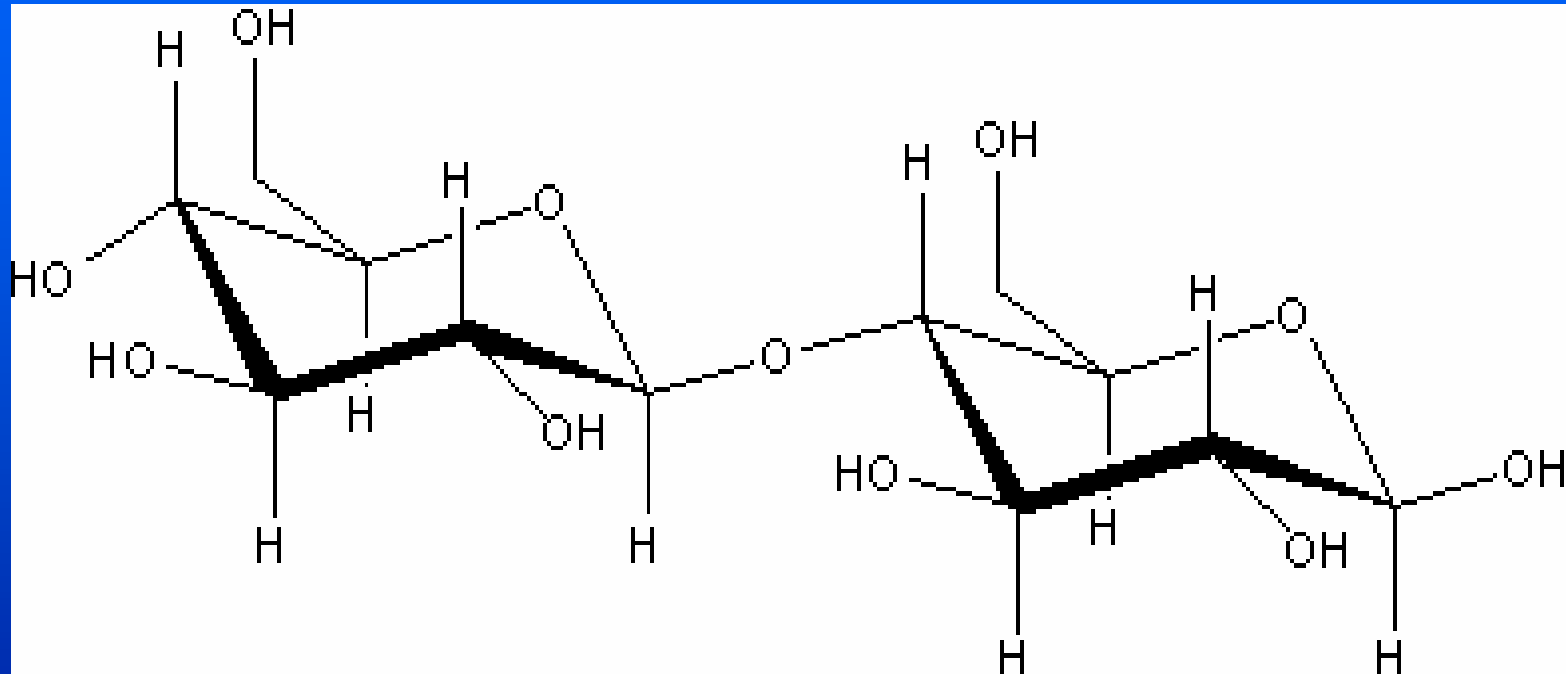
Two possible pathways for LCT mechanism

*Ying et al., *Angew Chem. Int. Ed.* **1999**, 38, 56-77

Organosulfonic Acid Groups



Oligosaccharide Hydrolysis



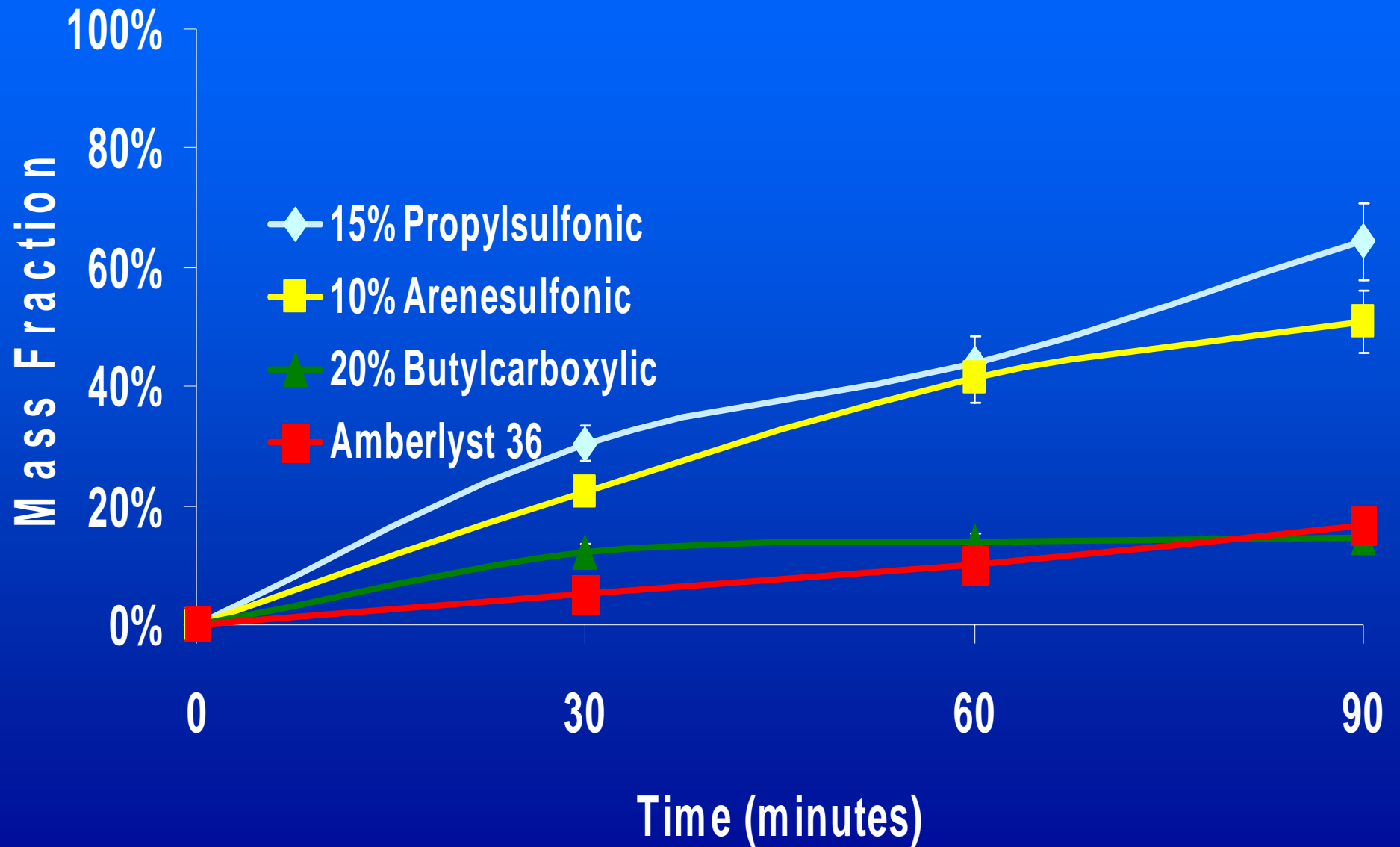
Textural Properties

Catalyst	Surface area (m ² /g)	Pore Diameter (Å)	Pore Volume (cm ³ /g)	Number of acid sites (meq)
7.5% Propylsulfonic	730	54	0.98	0.8
15% Propylsulfonic	765	62	1.27	1.1
10% Arenesulfonic	805	56	1.14	0.9
20% Butylcarboxylic	560	54	0.78	1.4

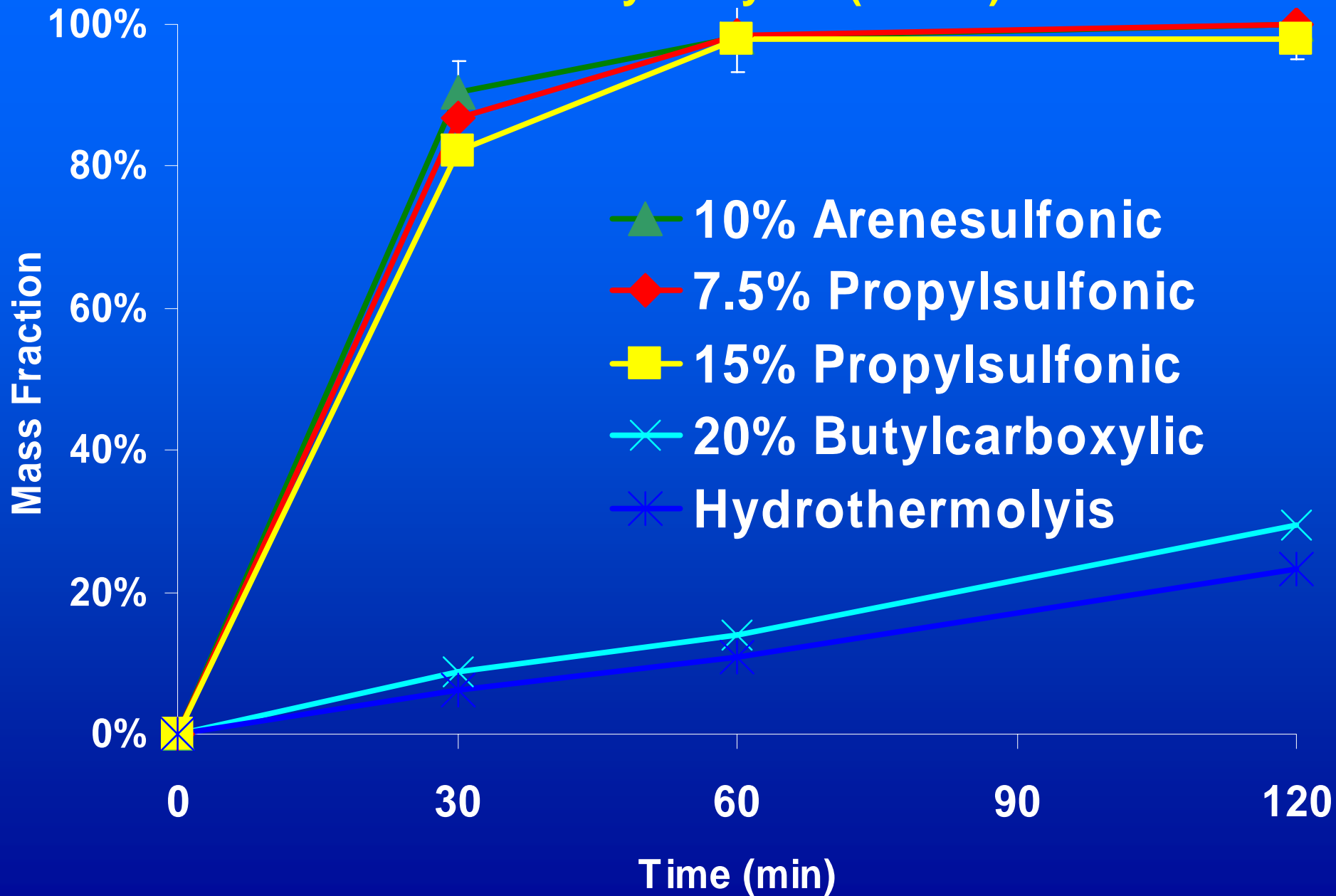
Chemical Properties

Catalyst	pH of Solution	pKa (by Gran Plot)	Carbon%	Sulfur%	Nitrogen%
7.5% Propylsulfonic	3.2	2.9	7.7	2.3	
15% Propylsulfonic	2.8	2.7	7.7	4.6	
10% Arenesulfonic	3.0	2.8	10.9	2.5	
20% Butylcarboxylic	4.9	4.6	14.0		0.4

Cellulose Hydrolysis (145 C)



Cellulose Hydrolysis (175 C)



Cellobiose Hydrolysis Activation Energy

Catalyst	Activation Energy (kJ/gmol)
7.5% Propylsulfonic Acid	133 +/- 13
15% Propylsulfonic Acid	113 +/- 17
10% Arenesulfonic Acid	137 +/- 20
20% Butylcarboxylic Acid	118 +/- 31
Sulfuric Acid*	110 +/- 29.6
Maleic Acid*	114 +/- 9.3

*N. S. Mosier, C. M. Ladisch, M. R. Ladisch, 2002, *Biotechnol. Bioeng.*, 79:17

Glucose Degradation Activation Energy

Catalyst	Activation Energy (kJ/gmol)
7.5% Propylsulfonic	67+/- 6
15% Propylsulfonic	65+/- 18
10% Arenesulfonic	73+/- 11
20% Butylcarboxylic	76+/- 20
Sulfuric*	118 +/- 37.5
Maleic*	72.6 +/- 22.5

*N. S. Mosier, C. M. Ladisch, M. R. Ladisch, 2002, *Biotechnol. Bioeng.*, 79:17

Acknowledgments

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